

CASE STUDY

Fe-Based Materials for Li-ion Batteries

Diminishing supplies of fossil fuels, together with the desire to reduce greenhouse gas emissions, has propelled electrochemical storage to the forefront of modern research.

In particular, Li-ion batteries have empowered consumer electronic devices and are now seen as having great potential for use in (hybrid)-electric-vehicles, where high power densities are essential.

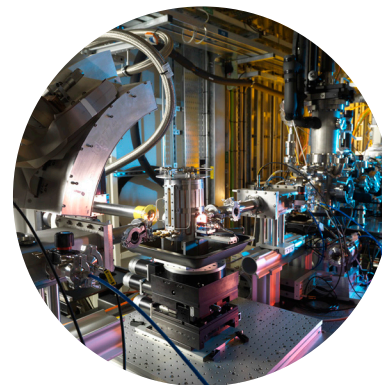
In the search for new positive electrodes to meet this demand, there has been a focus on polyanionic compounds and how they can be manipulated to control the voltage of the transition metal redox couple.



The Challenge

Scientists from France, in collaboration with researchers from the UK, have investigated the structure and performance of the triplite form of $\text{Li}(\text{Fe}_{1-\beta}\text{Mn}_{\beta})\text{SO}_4\text{F}$ as a potential Li-ion battery material.

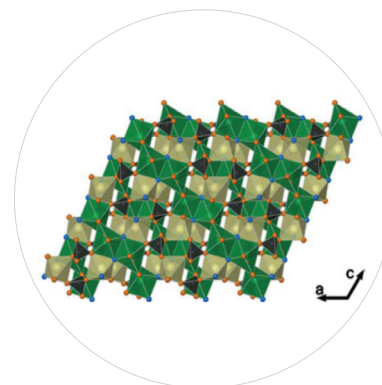
Intensive studies have shown that this phase exhibits the highest $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox voltage of any inorganic compound to date, but the complex interplay between structure, properties, and function still required clarification to ensure that the potential was not related to the Mn ions. Many available techniques employ *ex situ* approaches and the challenge is to examine these battery materials under their operating conditions.



The Solution

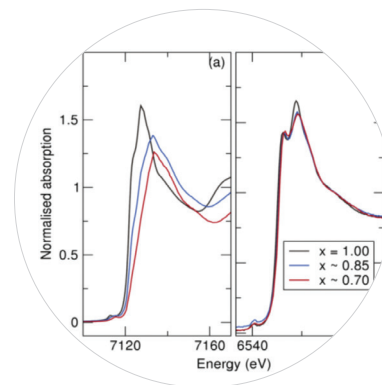
X-ray Absorption Spectroscopy (XAS) is an ideal technique for *in situ* local structure and oxidation state studies on Fe-based materials, as it enables researchers to probe the changes that occur in materials during electrochemical cycling without affecting the electrolyte, carbon, or binder that are used to construct functioning cells.

Investigators performed XAS measurements at the Fe and Mn K-edges to investigate the oxidation state of Fe and Mn in $\text{Li}(\text{Fe}_{1-\beta}\text{Mn}_{\beta})\text{SO}_4\text{F}$ during Li de-insertion in an operating battery cell.



The Benefits

The *in situ* measurements performed on an operating battery cell revealed that the iron undergoes an oxidation state change from $\text{Fe}^{3+}/\text{Fe}^{2+}$ during Li de-insertion, while there were no notable changes in the Mn K-edge. These results reveal the iron to be the electrochemical workhorse of this system, with the manganese complicit in the structural transformation to the triplite phase.



“Our studies performed at the B18 Core EXAFS beamline at Diamond tracked the changes occurring in the triplite phase $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{SO}_4\text{F}$ during battery cycling, revealing the iron to be the electrochemically active species in this material and confirming that the only role of manganese was to promote the structural change to the triplite over the tavorite phase.

These kinds of local structure analyses have afforded us insight into the reactions occurring in battery materials, allowing us to probe in greater detail the structure-property-function relationship in these important materials.”

Dr Serena Corr, University of Glasgow (Inset image, Dr Brent Melot)



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